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(71) Applicant

Bethlehem Steel Corporation, (USA—Delaware), 701 East Third Street, Bethlehem, PA 18017, United States of America

(72) Inventors

Robert H. Herron,
Bernard A. Indelicato

(74) Agent and/or address for service,

Eric Potter & Clarkson,
14 Oxford Street,
Nottingham,
NG1 5BP

(54) Silicon carbide refractories

(57) Silicon nitride bonded silicon carbide refractories having improved resistance to corrosion caused by alkali attack and retention of hot strength at temperatures of about 2400°F (1315°C) are made by a method in which initially a base mix is made. The base mix contains between about 80 and 90 weight percent silicon carbide particles of which at least 60 weight percent have a size consist of -6 m by $+140\text{ m}$ (-3.4 mm by $+105\text{ mm}$) and not more than 40 weight percent have a size of -140 m (-105 mm) and between about 10

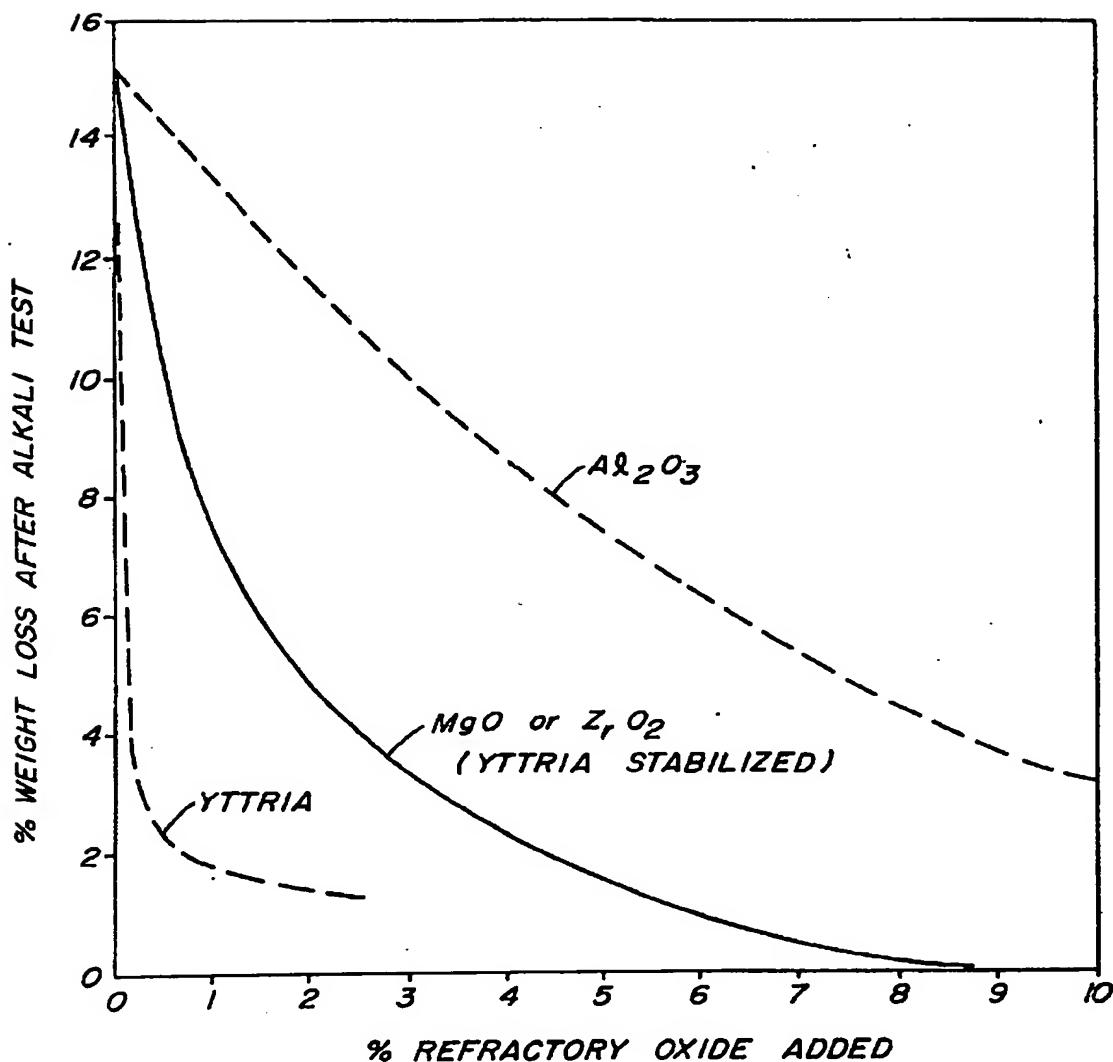
and 20 weight percent elemental silicon particles, substantially all of which have a size of -200 m (-0.074 mm). Between about 1 and 4 weight percent of fugitive binder, 4 and 8 weight percent water and 0.5 to 10 weight percent particles of at least one refractory oxide including magnesia, yttria-stabilized zirconia, yttria and alumina, substantially all of which are -150 m (0.084 mm) are blended into 100 weight percent of the base mix. The shaped blended mix is dried prior to being fired by a pre-determined firing cycle and are cooled to a desired temperature in the presence of the gaseous nitrogen atmosphere.

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FIGURE - EFFECT OF REFRACTORY OXIDE
ADDITION ON RESISTANCE TO
ALKALI CORROSION



SPECIFICATION
Silicon carbide refractories

This invention is directed to silicon nitride bonded silicon carbide refractories which are characterized by improved resistance to corrosion caused by alkali attack, retention of their natural 5 abrasion resistance and retention of their strength at elevated temperatures and to a method for manufacturing the refractories. The invention is in particular directed to such bonded refractories which are used in lining the interior surfaces of metallurgical furnaces.

Silicon carbide particles are used to manufacture refractories which have high strength at high 10 operating temperatures, have excellent abrasion resistance, are resistant to large rapid fluctuations in temperature and have high coefficients of heat transfer. Because silicon carbide refractories have excellent thermal conductivity, are abrasion resistant and retain their hot strength, they are particularly 15 useful in metallurgical furnaces, for example iron-making blast furnaces, aluminum refining furnaces and the like. Unfortunately, silicon carbide refractories are susceptible to early failure because of variable resistance to corrosion caused by alkali attack.

15 In an effort to overcome the susceptibility of silicon carbide refractories to corrosion due to alkali attack, it has been suggested that the silicon carbide refractories be bonded by one of several bonds, for example carbon bonds, silicate bonds, silicon nitride and/or silicon oxynitride bonds. Carbon bonds produced by adding pitch or resins to the silicon carbide grains are very susceptible to oxidation during 20 use. Silicate bonds produced by adding clay or clayey materials to the silicon carbide grains become soft and melt at high temperatures thereby adversely affecting the strength of the refractories at high 25 temperatures. Silicate bonds are also highly susceptible to failure due to corrosion caused by alkali attack. Silicon nitride bonds in the silicon carbide refractories do improve their high temperature strength, but their resistance to corrosion caused by alkali attack has been erratic.

It is the primary object of this invention to provide silicon nitride bonded silicon carbide 25 refractories characterized by retention of their natural abrasion resistance; retention of their hot strength at temperatures of about 2400°F (1315°C), improved resistance to corrosion caused by alkali attack and which are less susceptible to process variables than commercially available silicon nitride bonded silicon carbide refractories.

It is another object of this invention to provide a method for manufacturing silicon nitride bonded 30 silicon carbide refractories which are characterized by improved resistance to corrosion caused by alkali attack and retention of their natural abrasion resistance and hot strength at temperatures at about 2400°F (1315°C), which method includes forming a base mix of coarse and fine particles of silicon carbide and fine elemental silicon particles, blending at least one refractory oxide taken from the 35 group consisting of magnesia, yttria-stabilized zirconia, yttria and alumina, plus water and a fugitive binder to the base mix; forming shapes from the blended mixture; drying the shapes; firing the shapes for a time at a temperature in a gaseous nitrogen atmosphere to form silicon nitride bonds and cooling the shapes in a gaseous nitrogen atmosphere.

It is another object of this invention to provide silicon nitride bonded silicon carbide refractories characterized by having consistently good resistance to corrosion caused by alkali attack, which 40 refractories can be used to line the inner surface of a metallurgical furnace, for example an ironmaking furnace or an aluminum smelting furnace and the like.

Summary of the invention

According to this invention, there are provided silicon nitride bonded silicon carbide refractories characterized by retention of the inherent abrasion resistance of silicon nitride bonded silicon carbide 45 refractories, retention of hot strength at elevated temperatures of about 2400°F (1315°C), and improved resistance to corrosion by alkali attack as evidenced by minimal weight loss due to solution of silicon nitride in molten alkali salts over a period of time. The refractories are made from a base mix containing between about 80 and 90 weight percent silicon carbide particles and between about 10 and 20 weight percent elemental silicon particles to which are added between about 1 and 4 weight percent of a fugitive binder, e.g. lignin or dextrin and the like, between about 4 and 8 weight percent water and between about 0.5 and 10 weight percent particles of at least one refractory oxide including magnesia, yttria-stabilized zirconia, yttria and alumina. At least 60 weight percent of the silicon carbide 50 particles have a size consist of -6 m by +140 m (-3.4 mm by +.105 mm) and not more than about 40 weight percent have a size of -140 m (-.105 mm). Substantially all of the silicon particles are -200 55 weight percent have a size of -200 m (-0.074 mm).

The refractories are manufactured by a method which includes:

(a) providing a base mix of between 80 and 90 weight percent silicon carbide particles, at least 60 weight percent of which have a size consist of -6 m +140 m (-3.4 mm by +.105 mm) and not more than about 40 weight percent have a size of -140 m (-.105 mm) and between 10 and 20 weight percent elemental silicon particles substantially all of which have a size of -200 m (-0.074 mm),

(b) adding to 100 weight percent of the base mix of (a) above and blending therewith in sequence:

(i) between about 1 and 4 weight percent of a fugitive binder, e.g., lignin, dextrin and the like,
(ii) about 4 and 8 weight percent water, and
(iii) between about 0.5 and 10 weight percent particles of at least one refractory oxide including magnesia, yttria-stabilized zirconia, yttria and alumina substantially all of which are -150 m (0.084 mm) in size,
5 (c) forming predetermined shapes from the mixture of step (b) by pressure impacting,
(d) partially drying the shapes at room temperature for a time, e.g. 24 hours, and then heating the shapes to between about 210°F (99°C) and 250°F (121°C) and holding the shapes at temperature for a time, e.g. 5 to 24 hours, to remove substantially all the water remaining in the shapes,
10 (e) placing the shapes in a chamber to be heated,
(f) heating the shapes to a temperature of between about 700°F (371°C) and 800°F (427°C) for a time, e.g. 0.5 to 2 hours, to remove substantially all the fugitive binder,
15 (g) increasing the temperature of the shapes according to a predetermined firing cycle in a gaseous nitrogen atmosphere to convert substantially all the elemental silicon into silicon nitride bonds which bind the silicon carbide particles, and
(h) cooling the shapes.

Figure of the Invention

The Figure is a graph showing the improved resistance to corrosion caused by alkali attack of the refractories of the invention.

20 Preferred embodiment of the invention

According to this invention there are provided silicon nitride bonded silicon carbide refractories characterized by improved resistance to corrosion caused by alkali attack, retention of hot strength at temperatures as high as about 2400°F (1315°C) while retaining the inherent abrasion resistance of silicon nitride bonded silicon carbide refractories.

25 The silicon nitride bonded silicon carbide refractories are manufactured from a base mix containing between about 80 and 90 weight percent silicon carbide particles and between about 10 and 20 weight percent elemental silicon particles. The silicon carbide particles include coarse particles and fine particles. The coarse particles constitute at least 60 weight percent of the silicon carbide particles and have a size consist of -6 m by $+140\text{ m}$ (-3.4 mm , $.+105\text{ mm}$). The fine particles constitute not more than about 40 weight percent of the silicon carbide and are substantially all -140 m (-105 mm). Substantially all the elemental silicon particles are -200 m (-0.074 mm) in size. All mesh sizes in these specifications and claims are United States Standard Sieve Sizes unless otherwise noted. All percentages are on a weight basis unless otherwise noted.

30 An amount of a fugitive binder, e.g., lignin, dextrin and the like and water, commensurate with good refractory practice is added to the base mix and blended therewith to bind the silicon carbide particles during subsequent processing prior to firing the refractories.

35 Between about 0.5 and 10 weight percent (based on 100 weight percent of the base mix) particles of at least one refractory oxide including magnesia, yttria-stabilized zirconia, yttria and alumina are mixed and blended with the base mix and binder and water. The refractory oxide particles should have a size consistent with good refractory formulating practice, which in the invention may be about -150 m (-0.084 mm).

40 The mixture thus formed is blended and formed into shapes of predetermined size by pressure impact techniques. The shapes are dried at room temperature for a time, e.g., 20 to 24 hours, and are then heated to a temperature, e.g., 220°F (104°C) for a time, e.g., 5 to 24 hours, to remove substantially all of the last portion of moisture remaining in the shapes.

45 The dried shapes are placed in a heating chamber, e.g., a muffle or a furnace, and are initially heated to a temperature of between about 700°F (371°C) and 800°F (427°C) in air at a rate of about $300^\circ\text{F}/\text{hour}$ ($167^\circ\text{C}/\text{hour}$) to $350^\circ\text{F}/\text{hour}$ ($194^\circ\text{C}/\text{hour}$). The shapes are held at temperature for at least about 1 hour to drive off the fugitive binder. The chamber is purged for a time, e.g. about 15 minutes, with 99.9 volume percent pure dry nitrogen gas. During the remainder of the firing cycle, a dry gaseous nitrogen atmosphere is maintained in the chamber. The shapes are then heated to a temperature of between about 1900°F (1038°C) and 2200°F (1204°C) at a rate of between about $300^\circ\text{F}/\text{hour}$ ($167^\circ\text{C}/\text{hour}$) and $400^\circ\text{F}/\text{hour}$ ($222^\circ\text{C}/\text{hour}$) and are held at such temperature for at least eight hours. The temperature in the chamber is then increased to between about 2200°F (1204°C) and 2300°F (1260°C) and the shapes are held at such temperature for at least twelve hours. The temperature in the chamber is then increased to between about 2600°F (1427°C) and 2800°F (1538°C) and the shapes are held at such temperature for at least four hours. The shapes are then cooled to a temperature of about 700°F (371°C) or lower in the chamber in a gaseous nitrogen atmosphere and are then removed from the chamber and cooled to room temperature in air. In the interest of economy, the gaseous nitrogen may be turned off when the refractories reach a temperature of 700°F (371°C).

50 During heating, the elemental silicon reacts with nitrogen to form substantially all silicon nitride bonds. However, some silicon may combine with oxygen and nitrogen to form silicon oxynitride bonds.

It is within the scope of these specifications and claims that when silicon nitride bonds are referred to, such bonds may also include silicon oxynitride bonds. The two types of bonds occur and are present in the silicon carbide refractory. Either the silicon nitride or silicon oxynitride bonds may predominate in the refractory, that is, the bonds may be substantially all silicon nitride bonds with a minor portion of silicon oxynitride bonds present or the bonds may be predominantly silicon oxynitride with a minor portion of silicon nitride bonds present. It is preferred to have substantially all silicon nitride bonds with a minor portion of silicon oxynitride bonds present.

5 While it is preferred to use substantially pure dry nitrogen gas as the gaseous atmosphere in the heating chamber during the processing steps, commercially available nitrogen gas, which may contain 5 up to about 5 volume percent moisture, may be substituted for the dry nitrogen gas.

10 It has been found that unstabilized zirconia is unsuitable for use in the manufacture of refractory of the invention. Unstabilized zirconia added to the base mix of silicon carbide particles and silicon particles causes the refractories made from the mix to swell and spall during processing thereby 10 producing poor refractories. On the other hand, calcia or magnesia-stabilized zirconia may be added to 15 the base mix to produce silicon nitride bonded refractories. However, such refractories expand and spall when reheated, i.e. during their use in a furnace, and are susceptible to early failure due to such 15 expansion and spalling. The cause of such spalling is not known but it is postulated that the calcium and magnesium ions migrate during reheating resulting in unstabilized zirconia being present in the refractories and it is the unstabilized zirconia which causes the swelling and spalling of the refractories.

20 It is, therefore, not desirable to use calcia or magnesia stabilized zirconia in the manufacture of silicon 20 nitride bonded silicon carbide refractories.

The addition of as little as about 2 weight percent magnesia or 2 weight percent yttria-stabilized zirconia which can contain about 8 weight percent yttria as a stabilizing phase or about 0.5 weight percent 25 yttria or 5 weight percent alumina to a basic mix containing silicon carbide particles and elemental

25 silicon particles produce silicon nitride bonded silicon carbide refractories which have improved 25 resistance to corrosion by alkali attack as measured by a decrease in weight loss as determined by an alkali test hereinafter described. Increasing the amount of the refractory oxide additions to 5 weight percent magnesia or 5 weight percent yttria-stabilized zirconia and 2 weight percent yttria and 10 weight percent alumina improve the resistance of the refractories to corrosion caused by alkali attack.

30 However, such increase in the amount of the refractory oxide may result in a decrease in the hot 30 strength of the refractories. Additions of up to about 5 weight percent magnesia or 5 weight percent yttria-stabilized zirconia, or 2.0 weight percent yttria or 10 weight percent alumina produce silicon nitride bonded silicon carbide refractories which have relatively good hot strength at about 2400°F (1315°C), however, larger additions of the refractory oxides with the exception of yttria have 35 deleterious effects on the hot strength of the refractories at 2700°F (1482°C) hence such large 35 additions are to be avoided. Large additions of yttria, for example up to 5 weight percent, may be made. However, in the interest of economy such additions should be about 0.5 to 2.0 weight percent.

The improved resistance to corrosion by alkali attack of the refractories is shown graphically in the 40 Figure of the invention. The Figure is a graph which shows the weight loss during alkali testing of 40 specimens, 1 inch by 1 inch by 6 inches (2.54 cm by 2.54 cm by 15.2 cm), cut from each of several refractories made with refractory oxide additions.

The specimens were prepared for testing by placing 8 specimens on graphite setters in each of 45 two trays. The specimens were spaced apart at least 1/8 inch (0.318 cm). About 0.4 pound (0.181 kg) of anhydrous potassium carbonate was placed under, between and atop each specimen. The two trays 45

were stacked atop each other and spaced apart by graphite supports. The trays were placed in a stainless steel muffle box. Coke breeze was packed around the specimens and around the trays to completely fill the muffle and provide a reducing atmosphere in the muffle. A thermocouple was placed 50 in the center of the muffle. The packed muffle was placed in a furnace. The furnace was heated at a rate of 350°/400°F (194°/222°C) per hour to heat the specimens to about 1700°F (926°C). The 50 specimens were held at such temperature for three hours. The muffle was furnace cooled to below about 600°F (315°C) and was reheated to about 1700°F (926°C) at the same rate as above and held at temperature for three hours. The muffle was furnace cooled to about 200°F (93°C), removed from the furnace and unpacked. The muffle was opened and the individual trays were placed in water flowing at the rate of about 1 gallon per minute, (3.8 l per minute) and at a temperature between about 55 110°F (43°C) and 150°F (65°C) to leach the alkali. The individual specimens were carefully removed and leaching continued for twenty-four hours.

The specimens were then subjected to standard ASTM C 885 (Mod) Standard to determine the modulus of elasticity and ASTM C 133 (Mod) Standard to determine the modulus of rupture and to a determination of the weight loss after alkali test.

60 As shown in the Figure the addition of small amounts of refractory oxide does have a dramatic 60 effect on reducing the susceptibility to corrosion by alkali attack as shown by the small percent weight loss when compared to the percent weight loss experienced by silicon nitride bonded silicon carbide refractories control specimens without any oxide additions. As seen on the graph, yttria-stabilized zirconia and magnesia have approximately the same effect on reducing the susceptibility of the

65 refractory to alkali attack as shown by the present weight loss. Additions of alumina have much less 65

effect on percent weight loss. Yttria has the greatest effect on decreasing the susceptibility of the silicon carbide refractory to corrosion caused by alkali attack. Additions of as little as about 0.5 weight percent yttria reduce the weight loss to about 17 weight percent and additions of about 2.0 weight percent yttria reduce the weight loss to about 0.9 weight percent. Additions of 2 and 5 weight percent yttria-stabilized zirconia reduced the weight loss from about 15.5 weight percent experienced by a standard silicon nitride bonded silicon carbide refractory which does not contain a refractory oxide 3.2 and 0.9 weight percent, respectively. The additions of 2 and 5 weight percent magnesia reduced the weight loss to about 5.8 and 1.9 weight percent, respectively. It required an addition of at least 5 weight percent of alumina to obtain an appreciable effect on the reduction of weight loss in the alkali test and to impart significant alkali resistance about 7.5 weight percent alumina should be used. 5

Although alumina additions appear to have the least effect on the resistance to corrosion caused by alkali attack, the alumina additions also have the least effect on the hot strength of the refractories at 2700°F (1482°C). 10

Silicon nitride bonded silicon carbide refractories have a modulus of rupture of as high as about 5500 psi (387 Kg/cm²) at a temperature of 2400°F (1315°C) and a similar value at a temperature of about 2700°F (1482°C). The addition of 5 weight percent magnesia results in a modulus of rupture of about 5200 psi (366 Kg/cm²) at 2400°F (1315°C). At 2700°F (1482°C), the modulus of rupture drops to about 2000 psi (140 Kg/cm²). The addition of 5 weight percent yttria-stabilized zirconia results in a modulus of rupture of about 1300 psi (91 Kg/cm²) at 2790°F (1482°C). The addition of 0.5 weight percent yttria results in a modulus of rupture of about 5800 psi (408 Kg/cm²) at 2700°F (1482°C). An addition of 10 weight percent alumina results in a modulus of rupture of about 5700 psi (401 Kg/cm²) at 2400°F (1315°C) and of about 4600 psi (323 Kg/cm²) at 2700°F (1482°C). 15

In a first specific example of the invention, a base mix containing 88 weight percent silicon carbide particles and 12 weight percent elemental silicon particles was made. The silicon carbide particles include 68.7 weight percent having a size between -6 m and +140 m (-3.4 mm and +.105 mm) and 31.3 weight percent having a size of -140 m (-.105 mm). The elemental silicon particles had a size of 100 weight percent -200 m (0.074 mm). To 100 weight percent of the base mix were added about 2 weight percent lignin fugitive binder, 5 weight percent water and 5 weight percent of 98.5 percent pure magnesia particles substantially all of which were -150 m (0.084 mm) in size. After each addition of binder, water and refractory oxide, the mixtures were blended for about five minutes. 20 The final mixture was formed into three refractory shapes having the dimensions 1 inch by 4-1/2 inches by 9 inches (2.54 cm x 11.4 cm x 22.8 cm). The shapes were made by impact pressing with impacting lasting for about six seconds. 25

The shapes were dried for 24 hours at room temperature and were then heated to 200°F (104°C) and held at temperature for 24 hours to remove substantially all the moisture. 30

The dried shapes were packed in a muffle and placed in a furnace and were heated according to the following schedule: 35

- (1) heating at a rate of 300°F/hour (167°C/hour) to 700°F (371°C) in air. Hold one hour to remove fugitive binder, 40
- (2) purging the atmosphere in furnace for 15 minutes at 700°F (371°C) with 99.9 volume percent pure dry nitrogen gas, and continuing to pass the dry nitrogen gas through the furnace during subsequent steps, 45
- (3) heating the shapes at a rate of 300°F/hour (167°C/hour) to 2000°F (1093°C)—hold at temperature for 8 hours,
- (4) heating to 2200°F (1204°C)—hold at temperature for 12 hours, 50
- (5) heating to 2600°F (1427°C)—hold at temperature for 4 hours,
- (6) cooling to 700°F (371°C),
- (7) turning off dry nitrogen gas, and
- (8) cooling shapes to room temperature in air. 55

Four test specimens, each 1 inch by 1 inch by 6 inches (2.54 cm by 2.54 cm by 15.24 cm) were cut from each refractory shape. The specimens were alkali tested as previously described and weight loss was measured. The results are shown as example 1 in Table I entitled "Comparison of Effect of Refractory Oxide Additions on Properties of Silicon Nitride Bonded Silicon Carbide Refractory", shown at the conclusion of the specific examples. 60

In a second specific example of the invention, the above procedure was followed except that wet nitrogen gas, which was produced by bubbling dry nitrogen gas through water at room temperature, was used during firing and cooling cycles (2) to (7). 65

A control test shown as example No. 7 in Table I, in which refractory shapes devoid of refractory oxide additions and following the procedure of the first specific example was run. 70

In a third specific example of the invention, the procedure described in specific example 2 was followed except that 5 weight percent yttria-stabilized zirconia was added to the base mix. 75

In a fourth specific example of the invention, the procedure described in specific example 2 was followed except that 5 weight percent alumina was added to the base mix. 80

In a fifth specific example of the invention, the procedure described in specific example 1 was

followed, however, the base mix contained 86 weight percent silicon carbide particles and 14 weight percent elemental silicon particles.

In a sixth specific example of the invention, the procedure described in the fifth specific example was followed except the atmosphere used in steps (2) to (7) was wet nitrogen gas.

5 In a seventh specific example of the invention, the procedure described in the fifth specific example was followed except 0.5 weight percent yttria was added to the base mix and is shown as example No. 8 in Table I. 6

Table I
Comparison of the effect of refractory oxide additions on the properties of silicon
nitride bonded silicon carbide refractory

Example no.	Refractory oxide added weight percent	Weight percent elemental silicon in base mix	Atmosphere in furnace	Fire properties den-g/cc	% porosity	Resistance to alkali attack wt. loss %
1	5-Magnesia	12.0	Dry N ₂	2.62	17.5	0.5
2	5-Magnesia	12.0	Wet N ₂	2.61	17.5	2.4
3	5-Yttria-Stabilized Zirconia	12.0	Wet N ₂	2.60	19.1	1.0
4	5-Alumina	12.0	Wet N ₂	2.60	18.0	6.6
5	5-Magnesia	14.0	Dry N ₂	2.83	16.5	3.1
6	5-Magnesia	14.0	Wet N ₂	2.64	16.4	2.2
7	—	12.0	Dry N ₂	2.58	17.7	26.8
8	0.5-Yttria	14.0	Dry N ₂	2.66	15.6	2.9

From the above comparison, it can be seen that silicon nitride bonded silicon carbide refractories made from a base mix and containing specific refractory oxides have far less loss of weight when exposed to attack by alkali than do such refractory which are devoid of the refractory oxide additions. The refractory shapes heated in wet nitrogen gas appear to have good resistance to alkali attack and when the specific refractory oxides were added the hot strength of the refractories remained high at about 2400°F (1315°C) but lower strengths were observed at temperatures of about 2700°F (1482°C). 5

Claims

1. Silicon nitride bonded silicon carbide refractories characterized by the fact that they are made from a base mix containing between about 80 and 90 weight percent coarse and fine particles of silicon carbide, at least 60 weight percent having a size consist of -6 m by $+140$ m (-3.4 mm by $+105$ mm) and the remainder being -140 m (-105 mm) and about 10 to 20 weight percent particles of elemental silicon substantially all of which are -200 m (0.074 mm) in size, to which is added a fugitive binder, water and about 0.5 to 10 weight percent of particles of at least one refractory oxide taken from the group consisting of magnesia, yttria-stabilized zirconia, yttria, and alumina substantially all of which are -150 m (0.084 mm) in size, the refractory having improved resistance to corrosion caused by alkali attack while maintaining retention of its original abrasion resistance and hot strength at elevated temperatures as high as about 2400°F (1315.5°C). 10
2. The silicon carbide refractories of claim 1 characterized by the fact that the particles of refractory oxide added to the base mix are yttria in amounts between about 0.5 and 5.0 weight percent. 20
3. The silicon carbide refractories of claim 1 characterized by the fact that the particles of refractory oxide added to the base mix are magnesia in amounts between about 2 and 5 weight percent. 25
4. The silicon carbide refractories of claim 1 characterized by the fact that the particles of refractory oxide added to the base mix are yttria-stabilized zirconia in amounts between about 2 and 5 weight percent. 25
5. The silicon carbide refractories of claim 1 characterized by the fact that the particles of refractory oxide added to the base mix are alumina in amounts of between about 5 and 10 weight percent. 30
6. A method for manufacturing silicon nitride bonded silicon carbide refractories having improved resistance to corrosion by alkali when compared to conventional silicon nitride bonded silicon carbide refractories, characterized by:
 - (a) providing a base mix containing between about 80 and 90 weight percent silicon carbide particles at least 60 weight percent having a size consist of -6 m by $+140$ m (-3.4 mm by $+105$ mm) and the remainder being -140 m (-105 mm) and 10 and 20 weight percent elemental silicon particles substantially all of which are -200 m (-0.074 mm), 35
 - (b) blending into 100 weight percent of the base mix in step (a) a fugitive binder, water and between about 0.5 and 10 weight percent particles of at least one refractory oxide taken from the group consisting of magnesia, yttria-stabilized zirconia, yttria and alumina substantially all of which are -150 m (-0.084 mm) to the basic mix,
 - (c) blending the mix for a time to obtain a uniform mix,
 - (d) forming the mix into desired shapes,
 - (e) drying the shapes,
 - (f) charging the shapes into a heating chamber,
 - (g) heating the shapes at a temperature to remove substantially all the fugitive binder,
 - (h) purging the atmosphere in the furnace with nitrogen gas,
 - (i) heating the shapes to a temperature for a time in the presence of nitrogen gas,
 - (j) cooling the shapes in the chamber in nitrogen gas,
 - (k) removing the shapes from the heating chamber, and
 - (l) air cooling the shapes. 45
7. The method of claim 6 characterized by the fact that the shapes in step (i) are treated by a cycle wherein:
 - (i) the shapes are heated to a temperature between 1900°F (1038°C) and 2200°F (1204°C) and are held at such temperature for between 7 and 10 hours,
 - (ii) the temperature of the shapes is increased to between 2200°F (1204°C) and 2300°F (1260°C) and the shapes are held at such temperature for between 10 and 14 hours,
 - (iii) the temperature of the shapes is increased to between 2600°F (1427°C) and 2800°F (1538°C) and are held at such temperature for at least 4 hours in a nitrogen gas atmosphere. 55
8. The method of claims 6 or 7 characterized by the fact that about 2 to 5 weight percent particles of magnesia are added to the base mix in step (b). 60
9. The method of claims 6 or 7 characterized by the fact that about 2 to 5 weight percent particles of yttria-stabilized zirconia are added to the base mix in step (b). 80

10. The method of claims 6 or 7 characterized by the fact that about 0.5 to 5.0 weight percent particles of yttria are added to the base mix in step (b).

11. The method of claims 8 or 7 characterized by the fact that about 5 to 10 weight percent particles of alumina are added to the base mix in step (b).

5 12. The method of claims 6 or 7 characterized by the fact that the nitrogen gas in steps (h), (i) and (j) is dry nitrogen gas.

13. The method of claims 6 or 7 characterized by the fact that the nitrogen gas in steps (h), (i) and (j) is wet nitrogen gas containing about 5 volume percent moisture.

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